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TITLE: SELF-DEVELOPMENT X-RAY FILM (SBIR 87.I)

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U.S. DEPARTMENT OF DEFENSE

**SMALL BUSINESS INNOVATION RESEARCH PROGRAM
PHASE 1 — FY 1987
PROJECT SUMMARY**

Topic No. 87-277

Military Department/Agency Army.

Name and Address of Proposing Small Business Firm

Energy Optics, Inc.
224 N. Campo
Las Cruces, NM 88001

Name and Title of Principal Investigator

Jean J. Robillard, Research Scientist

Proposal Title

SELF-DEVELOPMENT X-RAY FILM

Technical Abstract (Limit your abstract to 200 words with no classified or proprietary information/data.)

This program is organized to demonstrate the feasibility of a non-silver Xray process to eliminate the need for special chemicals and a daylight developing machine for Army field dental application. This process will be compatible with current Xray equipment. The important objectives of Phase I are to investigate and demonstrate that an Xray picture using existing Xray equipment, no chemicals processing is necessary, insensitivity to light.

Anticipated Benefits/Potential Commercial Applications of the Research or Development

The application spans the entire field of Xray technology including industrial. Time, money, effort and frustration could be saved by this product which could revolutionize the industry.

List a maximum of 8 Key Words that describe the Project.

X-RAY, RADIOGRAPHS, FILM, EMULSIONS, DEVELOPMENT, NON-SILVER

I. INTRODUCTION

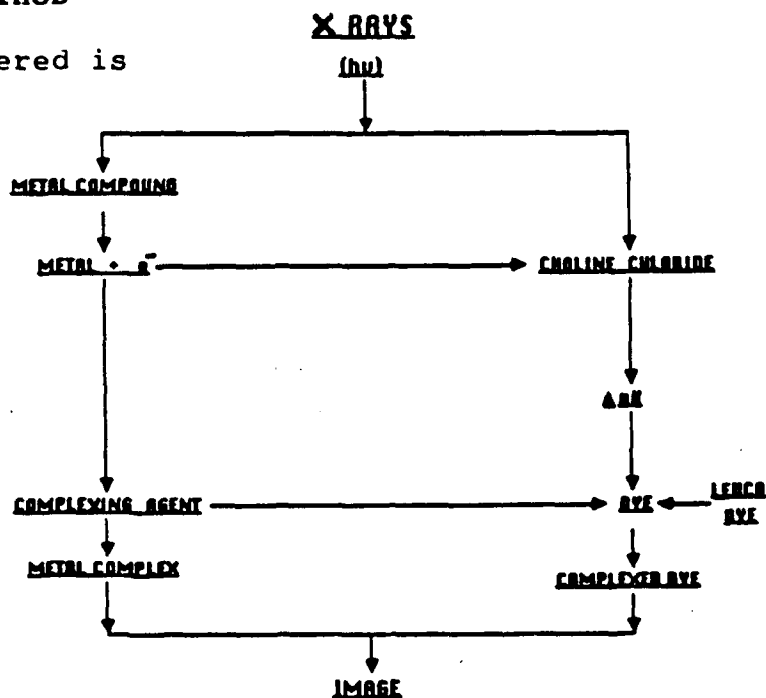
This final report covers the activities of Energy Optics, Inc. on the development of New Recording Materials for X-Rays during the period August 15, 1987 to February 15, 1988.

The main objective during Phase I was to prove the feasibility of a recording mechanism for X-Rays using high yield photodissociation of Choline Chloride. In doing so an objective was to obtain black images with acceptable contrast and a short development time. A number of complex mechanisms were involved in the formation of the image. These complex mechanisms were introduced in logical steps on a trial basis with proof of feasibility being the primary goal, before making a major commitment of funding. This trial basis procedure is not necessarily the most desirable and proper methodology for the development of a new process, assuming availability of unlimited funding, but was considered the most practical methodology under the circumstances; however, the results at this stage of development are by no means near optimization. The final product may not resemble the actual sample materials. The actual radiographs are highly encouraging, and good black images were obtained with sensitivity superior to silver halide films without screen. The emulsion is not sensitive to light and requires only heat development. The primary goal of proving feasibility was met with little expenditure of funding by comparison with most research tasks.

It is believed that stepwise optimization of the current phenomenon leading to the image if funded as a Phase II project will result in a highly usable alternative to silver halide emulsion, with major advantages for most applications.

II. PRINCIPLE OF THE METHOD

The approach considered is as illustrated:

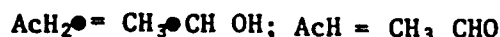
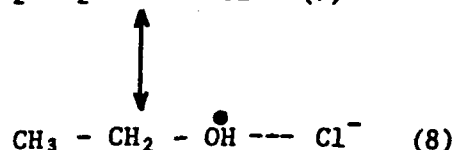
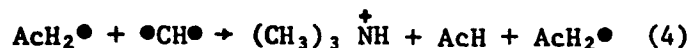


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A. Use is made use of the extreme sensitivity of choline chloride (¹) for ionizing radiation and electrons.

The product decomposes in trimethylamide and acetaldehyde under a chain reaction according to (²):

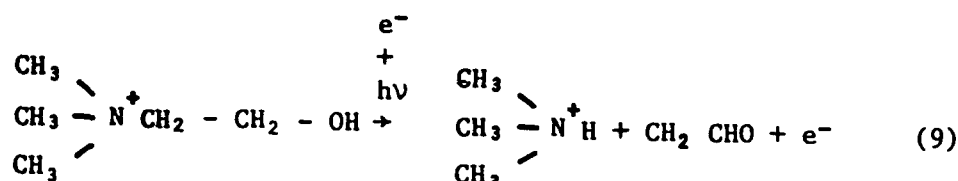


Initially the radiation (or electrons) acts to excite a choline chloride molecule.

The excited molecule has outbounding orbitals that lead to the fissure of the nitrogen to methylene bond. After the breaking of this bond the radical fragment are stabilized by hydrogen bonding and crystal cage effect. The ethanol fragment of the biradical can be observed by ESR. The $(\text{CH}_3)_3 \text{N}^{\text{O}+}$ is not seen because of excessive broadening by the main protons. The AcH_2 radicals are not seen because of their very low concentration. The observed radical reacts either with its cage (to propagate the decomposition reaction) or terminates with another radical that propagates into the vicinity.

The sensitivity of the photodissociation process expressed as the number of radicals produced by 100 eV absorbed is as high as 55,000. This represents a high amplification process involving chain reaction, which can compete favorably with silver halide process after development. It also has the advantage of not being sensitive to visible light.

B. The basic image formation is related to the change in pH which accompanies the reaction:



The reaction (9) is initiated directly by absorption of X-Rays, but also indirectly by absorption of Auger electrons generated by metal salts under the influence of the same radiation. Both phenomena contribute to the change of pH.

The first step in imaging is the oxidation of a leuco-dye into its colored form. Concurrently, the photolyzed metal salt in presence of a complexing agent provides a metal complex with deep color which increase the optical density of the dye. The oxidized leuco-dye can itself react with the complexing agent forming a dye complex which also increases the density.

To summarize, a high optical density image can be the result of the concurrent creation of:

- (a) an oxidized leuco-dye.
- (b) a dye complex.
- (c) a metal complex.

All this is initiated by the primary absorption of X-Ray, with amplification (chain reaction) and the secondary absorption of Auger electrons resulting from the absorption of the X-Ray by metal salts in the emulsion.

III. PREPARATION AND PROPERTIES OF SENSITIVE EMULSIONS

The original intent was to prepare the emulsion on a transparent substrate which eventually will be our final goal. We selected compounds which were known to work for the individual step considered.

Over twenty compositions have been designed. Ten of the compositions were listed in report No. 5 and are listed again in an appendix to this final report.

The three formulations which have given the best results are as follows:

S - 9 - 88

Cobalt Acetate	6.5 g.
Nitric Acid (10 solution)	13 g.
Water	66 ml.
Ammonium Oxalate	6.5 g.
Hexamethylenetetramine	13 g.
Urea	13 g.
Choline Chloride (a)	6 cc.
Leuco Crystal Violet (b)	6 cc.
Polyvinylalcohol (c)	20 g.
Tergitol	4 drps.

S - 20 - 88

Mercury Acetate	10 g.
Nitric Acid (10% solution)	10 g.
Water	100 ml.
Ammonium Oxalate	10 g.
Leuco Crystal Violet (b)	10 ml.
Choline Chloride (a)	10 ml.
Polyvinylalcohol (c)	30 g.
Tergitol	4 drps.

S - 14 - 23 - 88 (Two layers)

A. Layer 1

Mercurous Nitrate	10 g.
Water	70 ml.
Ammonium Oxalate	10 g.
Hexamethylenetetramine	10 g.
Choline Chloride (a)	10 cc.
Leuco Crystal Violet (b)	10 cc.
Polyvinylalcohol	30 g.
Tergitol TMN6	4 drps.

B. Layer 2

Mercuric Chloride	10 g.
Ethanol	40 cc.
Ammonium Oxalate	1.2 g.
Water	30 cc.
Urea	20 g.
Choline Chloride (a)	10 cc.
Leuco Malachite Green	10 g.
Polyvinylpyrrolidone (d)	50 g.
Tergitol TMN6	4 drps.

- (a) Saturated Solution in ethanol.
- (b) Saturated solution in ethanol.
- (c) 15% Solution in water.
- (d) 40% Solution in ethanol.

IV. PRELIMINARY RESULTS

1. Exposure

Exposures were made using a tungsten source with 1 mm. Al filter at 50 KV, 20 mA and resp. 1, 5 and 10 sec. exposure times.

2. Development

Proper thermal development equipment has been difficult to obtain. Existing equipment for commercial processes do not appear to be suitable for the New X-Ray Process, without modification. A Dry Silver Processor may be the most appropriate but time restraints prevented a full evaluation of available processors from Honeywell and 3M, even though a processor was supplied on a loan basis by Honeywell. It is anticipated that it will be necessary to design some equipment adapted to the requirements of the process. A steep temperature gradient up to 160° C is required followed by immediate cooling. The limited equipment tested for development included:

- a. Hair Dryer.
- b. 3M Thermofax Printer "Secretary".
- c. 3M Copy Mite 1.
- d. Drum Dryer: Arkay Dual Dri 150.
- e. Honeywell Thermal Processor

Only a and d provided significant results, c needed 6 passages at maximum temperature.

The following qualitative results from thermal development can be assessed (at the present time):

- A. Hot air (blower) provides: quick development but very difficult to control. Has a tendency to overdevelop or burn the emulsion (see Fig. 1). When the image appears it is already too late to stop the development process. There appear to be very little margin between no development and overdevelopment.
- B. Infrared. Here again, it is a question of speed and immediate cooling when the image appears. Cumulative heating (several passages) seems to result in poor contrast (see Fig. 2).
- C. Hot Drum (Drum Dryer) with air cooling. This solution has given the best results so far (see Fig. 3). The equipment (d) was run at maximum temperature and maximum speed.

3. Sensitivity

By not being able to control the development parameters we cannot appreciate the sensitivity of the system. However, it has been already found that images of relatively good quality can be obtained under the following conditions:

Source: W, 50 KV, 20 mA.
Exposure Time: < 1 sec.
Develop Temperature: 160° C. Approx.
Develop Speed: < 1 sec.

We also know that the materials and composition of the emulsion are far from being optimized.

Fig. 1 to 4 are representative of the state of development to the end of the Phase I.

Fig. 1, represents human teeth. The sensitive emulsion corresponds to the formulation S-14-23-88. The exposure conditions were:

Exp. Time: < 1 sec.
Source: Tungsten, 50 kv, 20 mA, Al 1 mm.
Distance: 20 cm.
Development: Hot air blower. Temperature evaluated at 160° C.

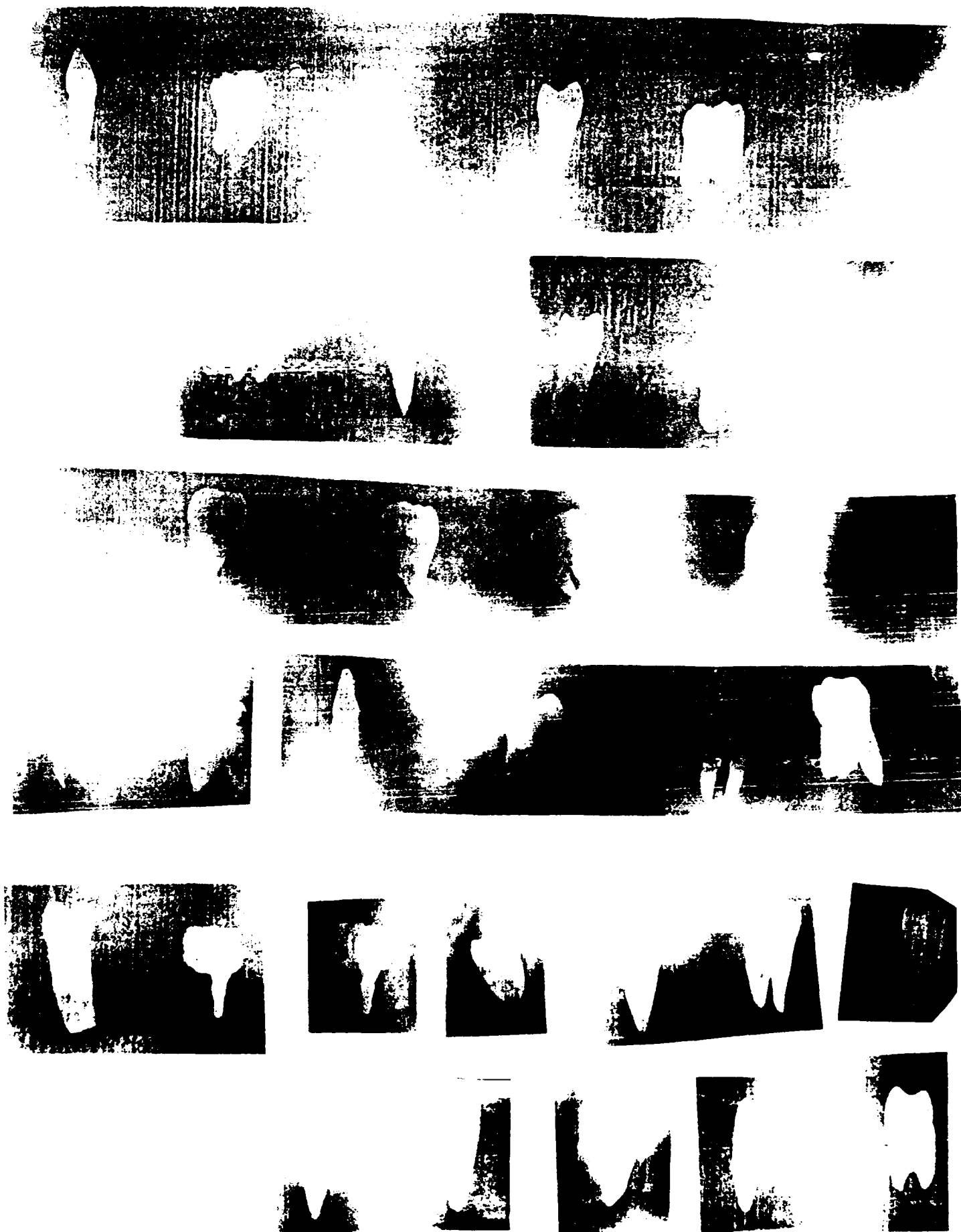


Figure 1



FIG. 2

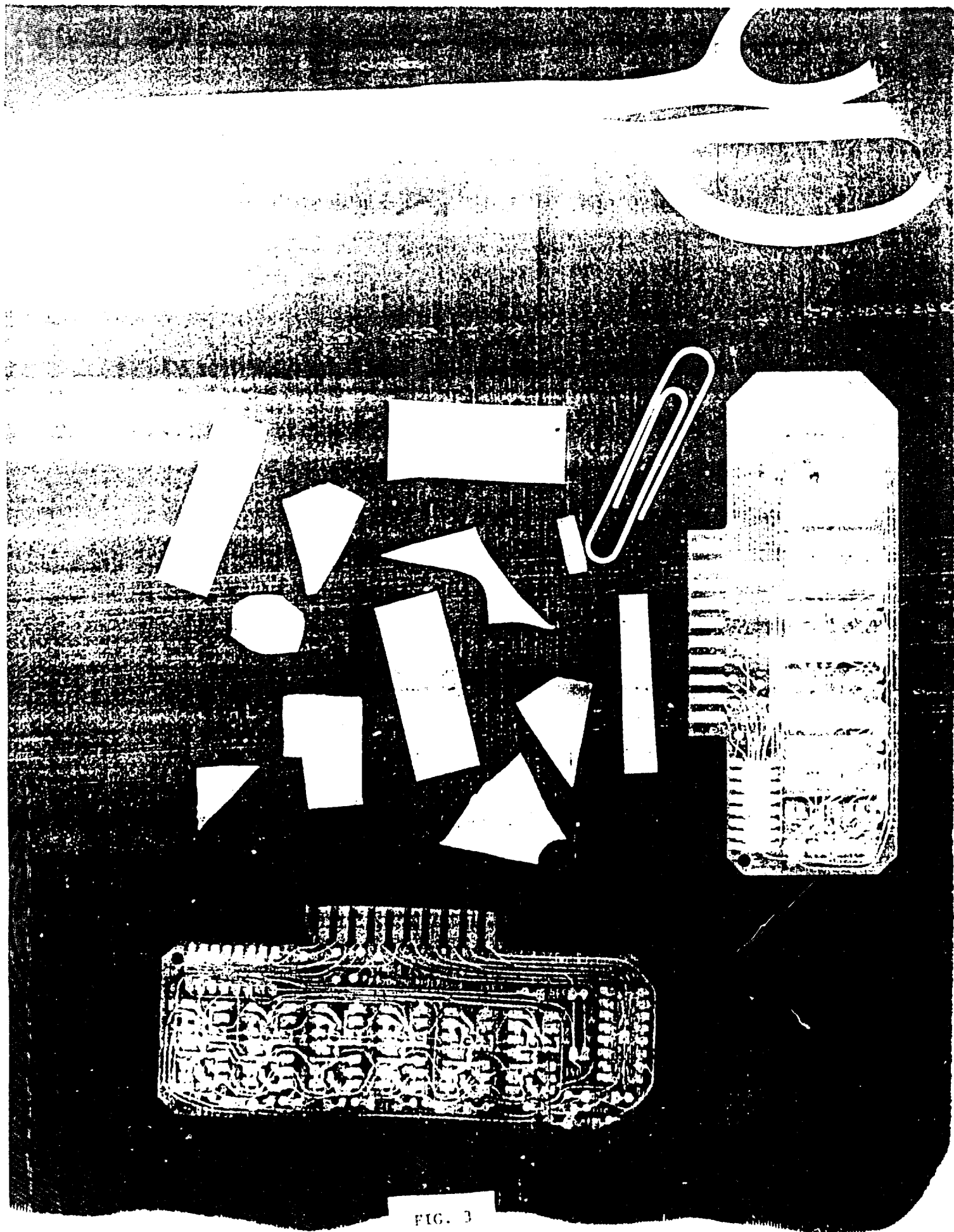
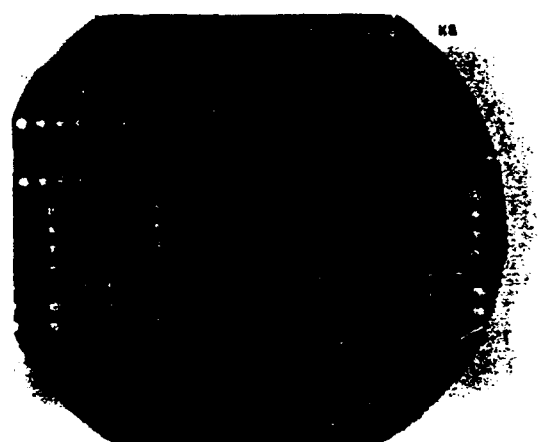


FIG. 3



10.1

V. CONCLUSION

Preliminary results have demonstrated the feasibility of the process; however, additional research is necessary for development of a workable process. To reach that goal a rational Phase II development program should be initiated. It would include:

1. Basic photoreaction mechanism.

A. Further study and optimization of the radiolysis of choline chloride precipitated in different binders.

B. Study of the imaging system:

Choline Chloride + Leuco-dye + pH buffer.
Choice of the leuco-dye, initial pH and binder.

C. Stability under different conditions of the initial component (choline Chloride, Leuco-dye).

2. Image Amplification Mechanism

A. Study of complexation of oxidized leuco-dye with organic complexants.

B. Study of complexation of oxidized leuco-dye with metallic salts.

C. Study of complexation of photoionized metallic salts with organic complexants.

3. Transparent Emulsions

Transparent emulsions would be better accepted in the medical field. It is therefore of major concern to develop an alternative emulsion on transparent substrate. Assuming the components and basic mechanisms remain the same, the metal salts will have to be introduced as solution in the binder which will decrease considerably the X-Rays absorption, the generation of reactive electrons and the extinction coefficient of the complexes generated from these metal salts. One way to increase the density of metal atoms and keep the transparency would be to introduce them as fatty acid metal salts (soaps). This solution would also bring the added advantage of a lower thermal development temperature.

4. Thermal Development

For a given exposure the quality of the picture will be very much depending upon the thermal development.

We have already determined qualitatively that heat would be transferred uniformly and during a short time. This

is only possible with a rotary drum heated at the development temperature and revolving at an optimum speed so that the contact of the drum with the emulsion can be controlled. An attractive solution appears to be microwave heating, using a linear applicator. The two basic advantages of such solution would be:

- A. Absorption of microwave (and heat generation) will be localized to the image forming material (no transfer). The energy necessary will be minimal (less than 10 watts).
- B. Possibility of drastic reduction in size (solid state microwave generator of a few cm³).

The main feature of the development of this process (Phase II) will then be:

- 1. Optimization of the chemical composition.
- 2. Development of a transparent emulsion.
- 3. Optimization of the thermal development.
- 4. Design and development of a thermal processor.

During the development of the Phase I processes the toxicity of the initial composition has been identified and will be eliminated during further development. This question relates only to metal salts which can easily be replaced by less toxic species without changing the mechanism of the process.

VI. BIBLIOGRAPHY

- (¹) B. M. Tolbert et al., J. Amer. Chem. Soc.,
75, 1867 (1953).
- (²) R. O. Lindblom et al., J. Amer. Chem. Soc.,
83, 2484 (1961).

APPENDIX

LIST OF EMULSIONS (From Report Number 5)

1. Emulsion No. 1

This emulsion was made in two parts :

A. The following composition was ball-milled for 24 hours :

ZnO	210 g.
Pliolite	55 g.
Acetone	115 g.
Toluene	120 g.
Sodium Oxalate	15 g.
Choline Chloride (¹)	21 g.

The resulting emulsion was coated on mylar sheet or baryta paper.

B. A second composition containing :

Cu (NO ₃) ₂	6 g.
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Acetamide	6 g.
Leuco Malachite Green ⁽²⁾	3 g.
Glycerol	1.5 cc.
Polyvinyl alcohol ⁽³⁾	4.5 cc.
Ethylalcohol	22.5 cc.
Tergitol	2 drops

was coated on top of the previous one.

2. Emulsion No. 2

Cobalt Acetate	30 g.
H ₂ O	160 g.
HNO ₃ (10%)	67 g.
Ammonium Oxalate	30 g.
Polyvinylalcohol ⁽³⁾	100 g.
Choline Chloride ⁽¹⁾	40 g.
Hexamethylene tetramine	67 g.
Urea	67 g.
H ₂ O	160 g.
Leuco crystal violet ⁽²⁾	20 g.

After homogeneization the emulsion is coated on a mylar sheet or baryta paper.

⁽¹⁾ Saturated solution in ethylalcohol.

⁽²⁾ 1% in ethylalcohol.

⁽³⁾ 15% in H₂O.

3. Emulsion No. 3

A.	Hg(1) nitrate	20	g.
	H ₂ O	140	cc.
	HNO ₃ (10%)	40	cc.
	Ammonium Oxalate	20	g.
	Polyvinylalcohol (³)	60	g.
	Hexamethylene tetramine	20	g.
	Choline Chloride (¹)	30	g.
	Tergitol	2	drops

After homogeneization the emulsion (A) is coated on a mylar sheet or a baryta paper.

B.	Cr (2) Chloride	20	g.
	Ethylalcohol	80	g.
	Polyvinylalcohol (³)	100	g.
	Ammonium Oxalate	3	g.
	H ₂ O	80	g.
	Urea	40	g.
	Leuco crystal violet (²)	20	g.

After homogeneization, emulsion B is coated on top of emulsion (A).

4. Emulsion No. 4

	Hg nitrate(1)	10	g.
	H ₂ O	50	g.

HNO_3 (10%)	20 g.
Ammonium Oxalate	10 g.
Hg nitrate(2)	0.5 g.
Polyvinylalcohol(³)	30 g.
Hexamethylene tetramine	20 g.
Urea	20 g.
H_2O	50 g.
Choline Chloride(¹)	20 g.
Leuco Malachite Green(²)	15 g.
Tergitol	2 drops

After homogeneization the emulsion is coated on a mylar sheet or a baryta paper.

5. Emulsion No. 5

HgCl_2 (2)	10 g.
Ethylalcohol	40 g.
Polyvinylpyrrolidone(⁴)	50 g.
Ammonium Oxalate	1.5 g.
H_2O	40 g.
Urea	20 g.
Choline Chloride(¹)	16 g.
Leuco crystal violet(²)	10 g.

After homogeneization the emulsion is coated on a mylar sheet or baryta paper.

(⁴) Solution 10% in ethylalcohol.

6. Emulsion No. 6

Hg acetate	10	g.
HNO ₃ (10%)	20	g.
H ₂ O	50	cc.
Ammonium Oxalate	10	g.
Polyvinylalcohol ⁽³⁾	30	g.
Hexamethylenetetramine	20	g.
Urea	20	g.
H ₂ O	50	g.
Choline Chloride ⁽¹⁾	20	g.
Leuco Malachite Green ⁽²⁾	15	g.

After homogeneization the emulsion is coated on a mylar sheet or baryta paper.

7. Emulsion No. 7

This emulsion is prepared in two parts (A) and (B) :

A.	CuCl	10	g.
	H ₂ O	70	g.
	HCl(50%)	10	cc.
	Polyvinylalcohol ⁽³⁾	40	g.
	Sodium p-toluene sulfinat	10	g.
	Choline Chloride ⁽²⁾	14	g.
	Lissapol	2	drops

After homogeneization emulsion (A) is coated on a mylar sheet or a baryta paper.

B.	CuSO ₄	20	g.
	Ammonium Oxalate	5	g.
	Urea	20	g.
	Polyvinylalcohol	60	g.
	H ₂ O	120	g.
	Leuco crystal Violet ⁽²⁾	18	g.
	Lissapol	2	drops

After homogeneization emulsion (B) is coated on top of emulsion (A).

8. Emulsion No. 8

	Hg (NO ₃) ₂	10	g.
	H ₂ O	70	g.
	HNO ₃ (10%)	20	cc.
	Ammonium Oxalate	10	g.
	Polyvinylalcohol ⁽³⁾	30	g.
	Hexamethylenetetramine	20	g.
	Choline Chloride ⁽¹⁾	15	g.
	Leuco Malachite Green ⁽²⁾	10	g.
	Tergitol	2	drops

After homogeneization the emulsion is coated on a mylar sheet or baryta paper.

9. Emulsion No. 9

HgCl ₂	10	g.
Polyvinylalcohol(³)	40	g.
Ammonium Oxalate	1.5	g.
H ₂ O	38.4	g.
Urea	20	g.
Choline Chloride (¹)	10	g.
Leuco crystal violet(²)	8	g.
Tergitol	2	drops

After homogeneization the emulsion is coated on a mylar sheet or baryta paper.

10. Emulsion No. 10

This emulsion is made in two parts :

A. The following composition is ball-milled for 24 hours :

TiO ₂	20	g.
Cariflex(20%)	22	g.
Toluene	76	g.
p-toluene sulfonic acid	1.5	g.
Urea	0.5	g.
Sodium Oxalate	1.5	g.
Choline Chloride(¹)	12	g.
Tergitol	2	drops